

STUDY OF THE PROPAGATION PROCESS OF A REACTION
IN SOLID PHASES

P.I.Bel'kevich and Ye.S.Osinovik

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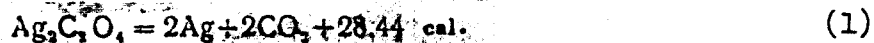
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P.I.Bel'kevich and Ye.S.Osinovik

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The propagation rate of reactions in solid phases was studied on the example of the change in electric conductivity of silver oxalate during thermal dissociation at 105 - 120°C. Tabulated data on decomposition after explosion and velocity-time curves for thermal dissociation are given to demonstrate that the explosive decomposition of silver oxalate on reaching the maximum reaction velocity proves its autocatalytic decomposition under the effect of a solid reaction product. The self-catalysis in topochemical reactions is attributed to the formation of a solid phase related with the crystal lattice of the initial substance. The motion of electrons along a wire, not connected with the crystal lattice of the oxalate, will not cause explosion.

In a number of investigations (Bibl.1 - 3) into the reaction kinetics of the thermal dissociation of silver oxalate, Bel'kevich, Volkova, and Yerofeyev showed that this reaction proceeds according to the equation



through the formation and growth of point nucleation loci of metallic silver which have a catalytic action on the rate of decomposition of the starting salt. A thorough study of the effect of various conditions on the course of the reac-

* Numbers in the margin indicate pagination in the original foreign text.

tion confirmed this conclusion. The kinetic regularities of the reaction of thermal dissociation of silver oxalate remained unchanged both during the decomposition of pure silver oxalate and during the decomposition of silver oxalate deposited on an inert carrier or taken in the form of a solid solution with sodium oxalate or else taken in the form of a mechanical mixture with inert materials at various ratios.

However, the concept of the course of the reaction through the formation and growth of three-dimensional silver nuclei, based only on kinetic laws, may be quite unfounded. This is all the more so since the literature contains different interpretations of this reaction. Thus, MacDonald (Bibl.4) at one time expounded the theory of the decomposition reaction of silver oxalate by a chain mechanism; Pavlyuchenko (Bibl.5, 6) in a number of papers maintained that self-acceleration of such reactions is not caused by the formation of nucleation loci of a new solid phase with an autocatalytic effect on the reaction velocity but rather by the destruction of the crystal lattice of the starting substance. Therefore, we attempted to find a direct experimental proof of the validity of the assumptions expressed here.

To solve the problem of the nature of the initial centers and to investigate the process of the propagation of the reaction from these centers, we studied the variation in electrical conductivity of silver oxalate during thermal dissociation.

In our opinion, a measurement of conductivity should have furnished new data permitting an evaluation of the form of the nucleation loci, of the reaction, and of the character of growth of the reaction nuclei. Three cases are theoretically possible.

1. The nucleation loci of the reaction occur as point formations. The

reaction nuclei grow at the same rate along three mutually perpendicular directions. Three-dimensional nuclei will form.

2. The nucleation loci of the reaction are linear formations (for example, the edge of a crystal). The nuclei grow in two mutually perpendicular directions, forming cylindrical nuclei. /150

3. At first, the face of the crystal reacts. The nucleation loci of the reaction are lamellae. The nuclei grow in one direction, forming plane-translational nuclei.

It is natural that the quantity of decomposed silver oxalate, before the appearance of conductivity of the crystal, will depend on the shape of the reaction nuclei. In the latter case (plane-translational nuclei), the salt will be conductive if the first lamella intersects the crystal. In the case of a three-dimensional development of the nuclei, the crystal will be conductive only when its entire surface is covered with metallic silver due to contact with a certain number of reaction nuclei.

The method of measuring the electric conductivity of a partially decomposed substance, to investigate the propagation process of a reaction in solids was used by J. MacDonald and R. Sandison (Bibl.7) who performed the thermal dissociation of pelleted silver oxalate to a certain degree of decomposition and measured the conductivity of the partially decomposed preparation at the temperature of liquid air. The experiments of these authors showed that, for unstable specimens of silver oxalate, a noticeable increase in conductivity is observed upon a 30% decomposition of the investigated silver oxalate and a 60% decomposition for a stable specimen. As a result, the authors concluded that the nuclei of silver are compact with respect to their formation.

According to the theory of "lamellar growth of nuclei" the conductivity

should be recorded at 25% decomposition for an unstable specimen and at 10%, for a stable one.

MacDonald and Sandison measured the conductivity only after completion of the experiment, which made it impossible to establish the exact limits of the appearance of conductivity of a crystal and rendered their conclusions unreliable. Therefore, in our work we investigated the conductivity during the entire time of thermal dissociation of silver oxalate in order to check the data of MacDonald and Sandison.

The pressure of carbon dioxide evolved during the reaction was measured manometrically. The metallic silver formed during the reaction of thermal dissociation of silver oxalate changed the conductivity of the pelleted starting product.

To preclude the possible influence of light on the reaction kinetics, all experiments were carried out in the dark; red light was used only for illuminating the display scopes.

Silver oxalate was prepared from chemically pure silver nitrate and sodium oxalate. The solution of silver nitrate, in an amount of 5 gm per 200 cc distilled water, was added by drops for 15 min under vigorous stirring (at 300 rpm of the mixer) to the solution of sodium oxalate (4 gm in 600 cc water). The temperature of the solutions during precipitation was kept at 25°C.

The experimental apparatus consisted of a high-vacuum device, a McLeod gage, and a reaction tube (Fig.1).

The wall of the reaction tube was provided with sealed-in leads to which platinum plate electrodes or probe (wire) electrodes were attached inside the reaction tube. The ohmmeter was attached to the leads at the outside of the tube.

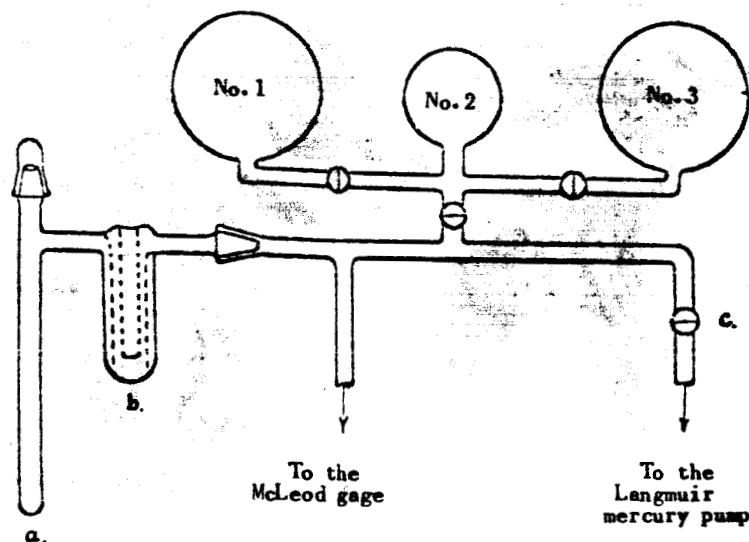


Fig.1 Diagram of the High-Vacuum Device
a - Reaction tube; b - Trap; No.1, 2, and 3 - Flasks.

The reaction tube was heated in an ultrathermostat filled with glycerol, whose temperature was automatically maintained within an accuracy of $\pm 0.2^\circ\text{C}$.

METHOD AND EXPERIMENTAL RESULTS

A sample of silver oxalate (about 50 mg) in the form of a pellet was placed between the platinum electrodes and clamped by insulated steel springs.

The specimen was placed in the reaction tube and the latter was connected to the device. A vacuum of the order of $10^{-5} - 10^{-6}$ mm Hg was created in the device along with the reaction vessels and the specimen was aged in the vacuum until the "in-leakage" at disconnected pump did not exceed an order of 10^{-5} mm Hg/min. After this, heating by the glycerol-filled ultrathermostat was started and this moment was taken as the beginning of the experiment.

The resistance of the investigated substance and the pressure of carbon dioxide were measured simultaneously during the experiment.

The maximum carbon dioxide pressure reached upon complete decomposition

of the sample did not exceed 1.5 mm Hg. The resistance was measured in the interval from 10 m Ω to 0.5 Ω .

The results of studying the decomposition kinetics of compressed silver oxalate at reaction temperatures of 105, 110, 115, and 120°C are given below. Most experiments were carried out to 80 - 100% decomposition of the starting substance.

To obtain the kinetic data on the thermal dissociation of silver oxalate and to compare them with the data of other investigators, we performed a series of experiments at 120°C on the thermal dissociation of silver oxalate powder.

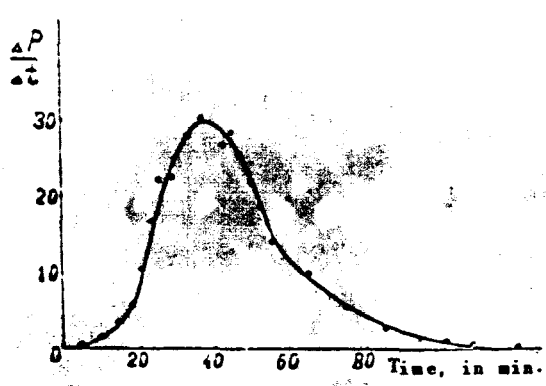


Fig.2 Velocity-Time Curve for Thermal Dissociation of Silver Oxalate

Figure 2 shows the curve of the reaction rate of the thermal dissociation of silver oxalate powder at 120°C, which in its overall slope is similar to the curves of autocatalytic reactions. During the first 10 min of decomposition /152 there is an induction period during which the reaction occurs at an immeasurably low rate, after which it increases, reaches a maximum after 34 - 36 min, and then drops to zero.

It is known from the literature (Bibl.1, 8) that the kinetic data on the thermal dissociation of silver oxalate, before reaching the maximum rate, are

satisfactorily described by the Kolmogorov-Yerofeyev equation and, during the entire reaction, by the Yerofeyev-Bel'kevich equation.

In view of the fact that the bulk of the experiments was carried out before onset of the explosive decomposition of the preparation at the instant of attaining maximum velocity, the mathematical analysis of the kinetic data was carried out by the Kolmogorov-Yerofeyev equation (Bibl.9, 10) $\alpha = 1 - \exp(-kt^n)$ which, in logarithmic form, reads

$$\log [-\log (1-\alpha)] = \log k + n \log t. \quad (1)$$

It is evident that if we plot $\log [-\log (1-\alpha)]$ on the ordinate and $\log t$ on the abscissa, we should obtain a straight line whose inclination to the abscissa gives the value of n , while the intercept with the ordinate gives the value of $\log k$.

The quantity n , as is known (Bibl.11), is equal to

$$n = \sigma + \frac{a}{3} \quad (2)$$

where

σ = number of successive stages, or number of electrons, required for formation of a stable nucleation locus of the reaction;

a = constant number, characterizing the form of the reaction nuclei and equal to 3, 2, or 1 (depending on the formation of three-dimensional, cylindrical, or plane-translational reaction nuclei).

It is evident from Fig.3 that the kinetics of the thermal dissociation of silver oxalate is well described by the Kolmogorov-Yerofeyev topokinetic equation.

Since, during the main investigation, it was necessary to use compressed silver oxalate, we carried out experiments to define the influence of pelleting on the reaction kinetics. It was established by corresponding experiments that the pressing of silver oxalate under our conditions has no noticeable effect on

the kinetics of thermal dissociation.

The main experiments with compressed silver oxide were carried out, as indicated above, at temperatures of 105, 110, 115, and 120°C while simultaneously measuring the kinetics of the process and the electric resistivity of the preparation.

The pellets of pressed silver oxalate were placed between platinum electrodes having plate or wire configuration ($d = 1.5$ mm).

The voltage at the terminals of the ohmmeter was 1.3 v and was constant regardless of the voltage of the electric current fed to the instrument.

Figures 4 and 5 show the kinetic data on the decomposition of pressed 153 silver oxalate placed between platinum plate electrodes. Simultaneously with the variation in reaction velocity, Fig.5 also shows the variation in electric resistivity ($\log R$) of the preparation during the reaction.

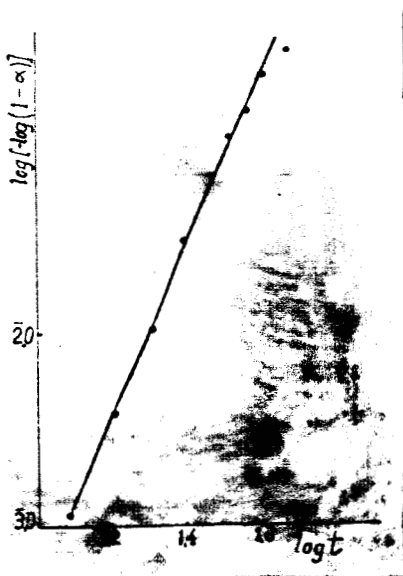


Fig.3 $\log [-\log (1 - \alpha)]$ as a Function of Time for Thermal Dissociation of Silver Oxalate

It is apparent from Fig.4 that, up to instant of explosion of the silver oxalate, the kinetics exactly obey the power law and the change in reaction

velocity in logarithmic form is expressed by a straight line. The values of n are virtually identical and equal to 4, i.e., the process of the formation of a stable nucleus is identical for various reaction temperatures. We see from Fig.5 that a marked drop in resistance in the pressed silver oxalate during decomposition is observed at the moment of maximum reaction velocity.

Similar results are obtained in experiments with platinum wire electrodes (Figs.6 and 7), which were carried out to determine the effect of the platinum electrode configuration on the reaction of thermal dissociation of silver oxalate.

Thus, it is established that the configuration of the platinum electrodes does not affect the process of thermal dissociation of silver oxalate.

In one of the experiments (No.47) on the thermal dissociation of pressed silver oxalate at 115°C placed between platinum wire electrodes, we were able to measure the gradual decrease in resistivity of the reacting silver oxalate from $10\text{ m}\Omega$ to $0.5\ \Omega$, followed by detonation of the preparation. The dependence of the resistivity of the preparation on the reaction time can be represented by the following Table.

TABLE 1

Time, in min.	10	20	50	55	56.5	57	57.5	57.7	58	58.5	59	60
Resistivity in Ω	10^7	10^7	10^6	800	130	70	40	32	24	17	10	Explosion

In another experiment (No.35) at 105°C we were also able to measure the gradual drop in resistivity of the reacting silver oxalate, plotted in Fig.8.

The reproducibility of parallel experiments is good, confirmed, for example, by Figs.9 and 10, for the reaction of thermal dissociation of silver

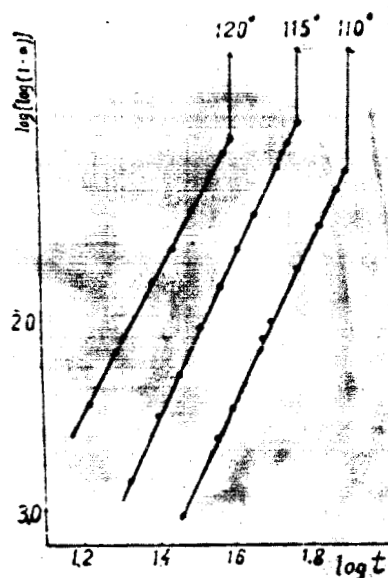


Fig. 4 Temperature Dependence of the Reaction Velocity (for Plate Electrodes)

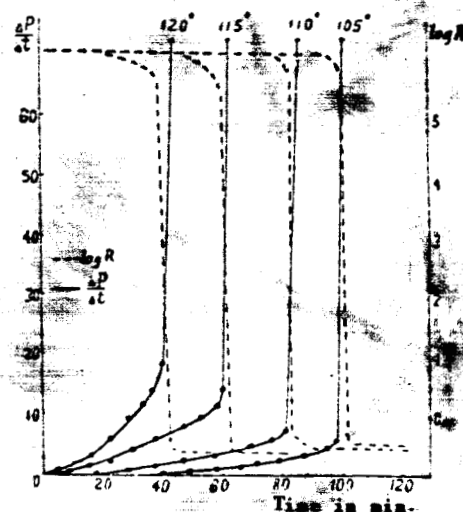


Fig. 5 Correlation between Reaction Velocity ($\Delta P / \Delta t$) and Logarithm of Resistance ($\log R$) on one Hand and Reaction Time (t) in the Temperature Range of 105 - 120°C on the Other (for Plate Electrodes)

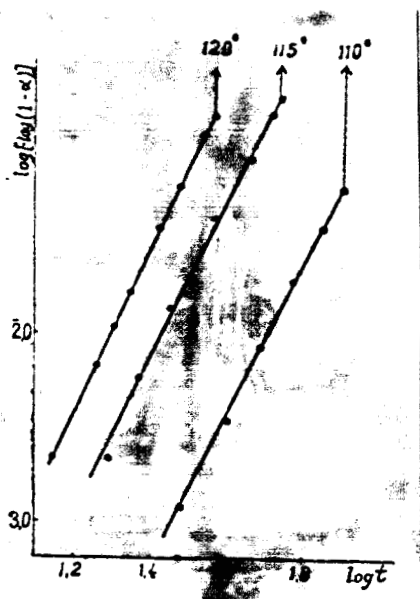


Fig. 6 Curves $\log [-\log (1 - \alpha)]$ vs. $\log t$ for Decomposition of Silver Oxalate at Various Temperatures (Wire Electrodes)

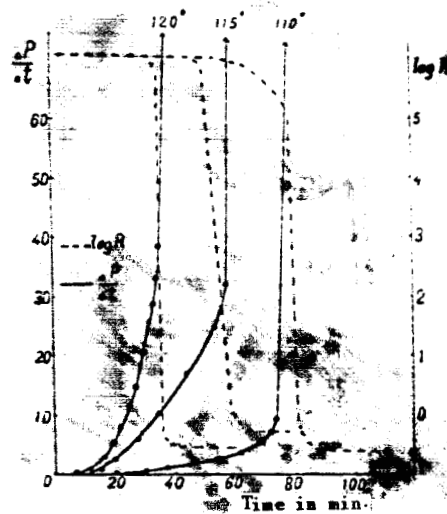


Fig. 7 Velocity-Time Curves and Logarithm of Resistance-Time for Thermal Dissociation of $\text{Ag}_2(\text{COO})_2$ at 110, 115, 120°C

oxalate at temperatures of 120 and 115°C.

DISCUSSION OF THE RESULTS

A characteristic feature of the experiments on the thermal dissociation of silver oxalate at temperatures of 105, 110, 115, and 120°C with simultaneous measurement of the resistivity of the reacting preparation is the explosive decomposition of silver oxalate at the instant maximum reaction velocity is 155 reached.

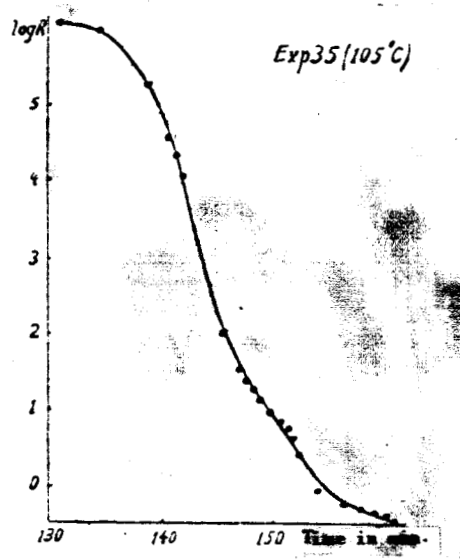


Fig.8 Correlation between Logarithm of Resistance and Reaction Time

Up to the reaction maximum, the kinetics of the thermal dissociation process obeys the exponential law $\alpha = 1 - \exp(-kt^n)$ with values of n close to 4.

From a kinetic analysis of $n = \sigma + 3$, where σ is the number of electrons required for the formation of a stable reaction nucleus, we concluded that in most of our experiments one electron, which in this investigated reaction is assumed to be silver ions, is needed for the formation of a stable nucleus (Table 2).

TABLE 2

No. of Test	Temperature of Experiment in °C	% Decomposition before maximum reaction velocity	% Decomposition after explosion of preparation	Values of n with respect to equation $\alpha = 1 - e^{-kn}$
21	120	17.0	48.7	4.57
22	115	18.5	69.3	5.0
23	110	17.0	40.3	4.0
24	105	18.7	89.8	5.6
26	120	30.0	81.2	4.7
33	115	21.8	78.6	4.1
34	110	19.5	68.6	4.0
36	105	18.5	52.6	3.7
38	120	23.3	67.7	3.9
39	110	18.0	80.7	4.0
40	115	21.9	70.8	4.1
47	115	27.6	70.4	3.8
48	110	24.5	77.7	3.7

The data in Table 2 show that, up to the velocity maximum, from 17 to 30% of the starting substance has time to react, and then the resistivity markedly drops and the preparation explodes.

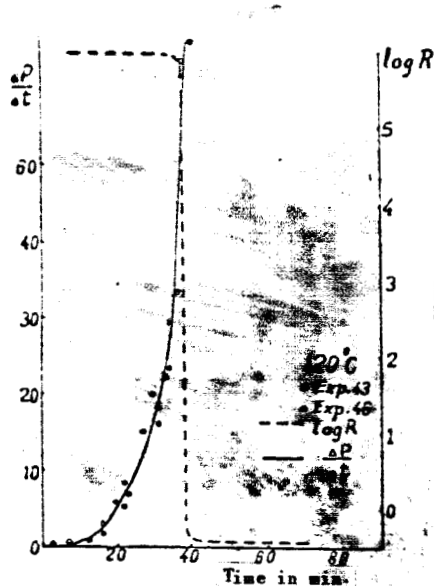


Fig.9 Reproducibility of Velocity-Time Curves and Logarithm of Resistance-Time for the Thermal Dissociation of Silver Oxalate (Wire Electrodes)

Thus, the following need be explained:

- 1) reason for the appearance of electric conductivity of the salt;
- 2) causes leading to the explosion of the unreacted part of the preparation.

Evidently, in the presence of such a quantity of the reaction product, silver oxalate becomes conductive as a result of the continuous coating of the surface of individual crystals or crystal aggregates by reaction nuclei. Numerous channels are formed with a low resistance along which the electric current is directed.

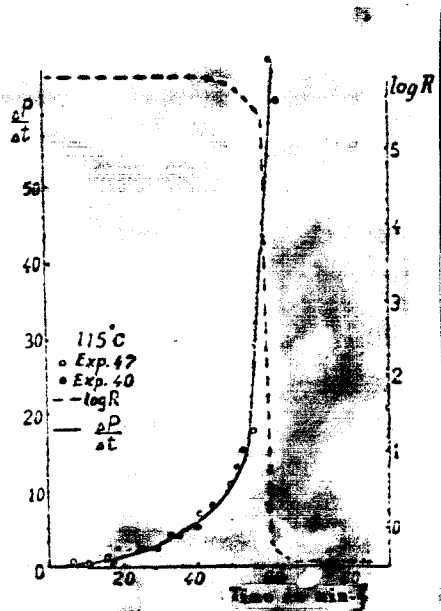


Fig.10 Reproducibility of Velocity-Time Curves and Logarithm of Resistance-Time for the Thermal Dissociation of Silver Oxalate (Plate Electrodes)

If the decomposition process of silver oxalate were to occur uniformly /156 over the entire mass of single crystals, then, as the calculations by MacDonald and Sandison (Bibl.7) indicate, the crystal would become conductive upon decomposition of more than 60% of the substance, whereas in reality this occurs at 17 - 30% decomposition.

Apparently, the decomposition of silver oxalate begins with the formation of numerous reaction nuclei on the surface of the crystal aggregates which, during three-dimensional growth, merge at the instant the maximum reaction velocity is reached, forming a continuous front of metallic silver.

One of the possible causes of the explosive decomposition might be electric breakdown. However, the following facts oppose this hypothesis (Bibl.12, 13):

1. For solid salts, the breakdown voltage of an electric force field, as is known, amounts to thousands of volts. We used an electric current of a comparatively low voltage and low strength ($V = 1.3$ v, $I = 0.4$ ma).

2. To produce breakdown it is necessary to ionize the gas gap and create a flux of ions or electrons, for which a field strength of the order of tens of kilovolt is required. In our experiments, we did not observe a change in current strength or in voltage, which remained constant during the entire experiment. The distance between the silver ions was of the order of 10^{-8} cm, which

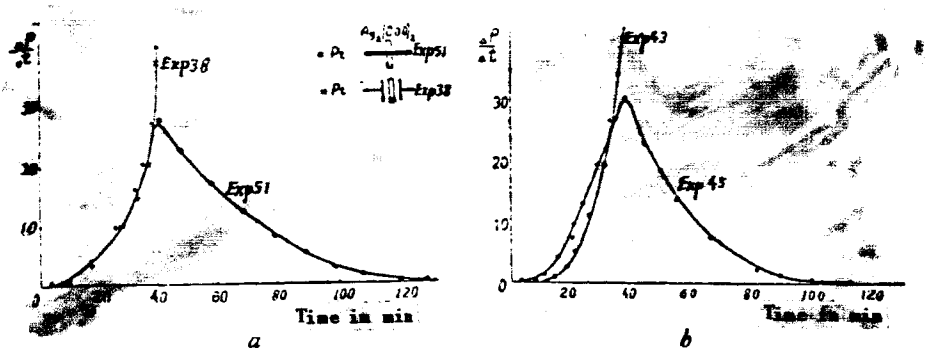


Fig.11a and b Kinetic Curves of the Thermal Dissociation of Silver Oxalate Placed between Plate Electrodes (Experiments Nos.38, 43) and Pressed around a Wire (Experiments Nos.51, 45)

permitted free passage of the electrons along the contacting silver particles, deprived of a charge but retaining a close-packed structure of the crystal lattice. Therefore, the explosion of silver oxalate at the maximum reaction

velocity upon contact of the three-dimensional nuclei must be due to other causes.

The explosive decomposition of silver oxalate under our experimental /157 conditions is, in our opinion, an important experimental proof for the autocatalytic action of the reaction product. As shown by P.D. Dankov (Bibl. 14, 15), the new solid phase is in a metastable state (in crystallochemical correspondence with the starting substance) while retaining the crystal structure of the initial substance.

At the maximum reaction velocity, individual nuclei of the new solid phase on the surface of the crystal aggregates form a continuous front of silver particles, which retain the structure of the crystal lattice of silver oxalate. A portion of the metallic silver is located at the interface of the two solid phases: silver-silver oxalate. Under the effect of a flux of electrons the reaction of thermal dissociation in conformity with the above-cited mechanism should occur instantaneously, which is also produced by the positive thermal effect $\text{Ag}_2 (\text{COO})_2 = 2\text{Ag} + 2\text{CO}_2 + 28.44 \text{ cal.}$

It is necessary to bear in mind that for the explosive decomposition of silver oxalate it is not a simple electron flux that is required but an electron flux passing over the silver particles, which latter are associated with the ions of the crystal lattice of the initial substance and are removed from it by a distance of the order of atomic spacings (10^{-8} cm).

The validity of this assumption is confirmed by the following data:

The results of several experiments are compared in Fig. 11a and b. In experiments Nos. 51 and 45, at 120°C , the silver oxalate was pressed around a platinum wire through which an electric current ($V = 1.3 \text{ v}$, $I = 0.4 \text{ ma}$) flowed during the entire reaction of thermal dissociation. No explosion took place.

The reaction proceeded quietly, the rate of decomposition gradually increased to a maximum and then dropped to zero. The velocity-time curve had a slope typical for autocatalytic reactions. On the other hand, in experiments Nos.38 and 43, at 120°C, with pressed silver oxalate placed between platinum electrodes, explosive decomposition of the preparation always occurred at the maximum reaction velocity.

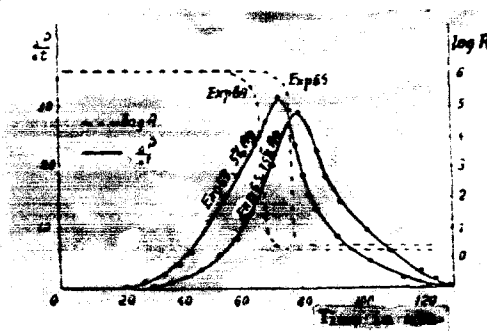


Fig.12 Velocity-Time Curves and Logarithm of Resistance-Time for the Thermal Dissociation of Silver Oxalate with Additions of Reaction Product

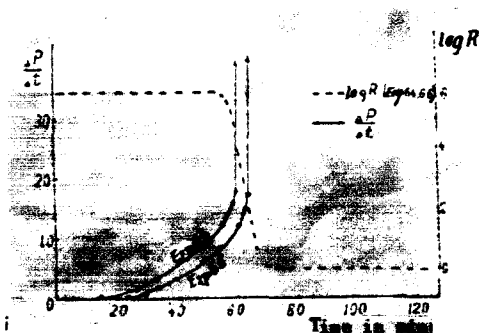


Fig.13 Velocity-Time Curves and Logarithm of Resistance-Time for the Thermal Dissociation of Silver Oxalate with Additions of Reaction Product

In most experiments, thermal dissociation of silver oxalate under the effect of an electric current led to explosion as soon as the preparation was 20 - 30% decomposed. If this process were accompanied by electric breakdown, then the silver oxalate with an addition of metallic silver (reaction product)

in an amount up to 20 - 30% would produce explosive decomposition upon passage of an electric current during the initial stage of the reaction.

However, the experiments on the thermal dissociation of silver oxalate /158 at a temperature of 120°C under the addition of silver (reaction product) in amounts of 5, 10, 15, 20, and 25% showed that the thermal dissociation is not accelerated (Figs.12, 13).

Apparently, metallic silver which has no bond with the crystal lattice of the reacting silver oxalate and which is introduced into the reacting medium from without, has no accelerating effect on the thermal dissociation of silver oxalate.

A shift in the maximum reaction velocity toward a larger time value can apparently be explained by the fact that the silver particles as an addition promote a rapid dissipation of the thermal energy of the exothermic reaction upon contacting the surface of the crystal aggregates.

In the experiments with additions of metallic silver, certain preparations did not lead to explosive decomposition of silver oxalate despite the fact that the resistivity of the reacting substance, long before reaching the maximum velocity, dropped to 0.5 - 0.6 Ω and an electric current passed through the preparation (Fig.12).

Figure 13, on the other hand, shows the kinetic data of the reaction occurring with an explosion at the maximum, when the resistivity of the reacting preparation ($\log R$) markedly dropped at this moment. This difference in the character of decomposition can apparently be explained by the position of the silver particles in the mixture with the oxalate.

If the particles of the introduced silver are distributed irregularly and make up a chainlet interrupted by individual particles of silver oxalate, then,

without reaching the maximum, the electron flux can pass through this chainlet without producing a noticeable effect on the kinetics of the thermal dissociation of silver oxalate. This case, in all respects, resembles the experiments Nos. 51 and 45 (Fig. 11a, b) where the silver oxalate was pressed around a platinum wire through which an electric current was passed.

In this case, when the particles of the introduced silver are distributed uniformly, separated by particles of silver oxalate, the electron flux can pass only along the surface of the crystal aggregates which, close to the maximum reaction velocity, will be covered by a layer of the reacted silver which is in crystallochemical correspondence with the silver oxalate. As a result, explosive decomposition occurs.

TEMPERATURE DEPENDENCE OF EXPLOSIVE DECOMPOSITION

/159

The results of explosive decomposition of silver oxalate are presented in Table 3.

TABLE 3

Reaction Temperature °C	Explosion time min.	Mean value of τ sec. to experiment	Explosion time based on equation $\tau = \frac{A}{T - C}$
105	102	102	105
110	86; 84; 78	81.6	76.8
115	60; 58; 62; 56	59.0	56.3
120	43; 37; 36	38.7	40.0

The data of Table 3 show that, at a 5°C rise in reaction temperature, the explosion time drops on the average by 20 min (Fig. 5).

If we plot $\log \tau$ on the ordinate, where τ is the explosion time of silver

oxalate in minutes, and $\frac{1}{T}$ on the abscissa, where T is the temperature of the experiment on the absolute scale, then we obtain a linear dependence between these quantities (Fig.14). It is evident that this dependence can be expressed by the equation

$$\log \tau = \frac{A}{T} - C \quad (3)$$

The numerical value of the constant is as follows:

$$A = 4 \times 10^3, C = 8.555.$$

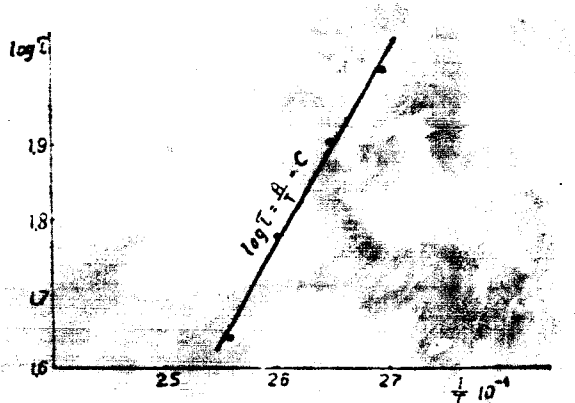


Fig.14 Applicability of the Equation $\log \tau = \frac{A}{T} - C$

CONCLUSIONS

1. The thermal dissociation of silver oxalate was studied at temperatures of 105, 110, 115, and 120°C under simultaneous measurement of the electric resistivity of the preparation during the reaction.

2. It was established that, during the reaction, a marked decrease in resistivity takes place accompanied by explosion of the preparation on reaching 160 the maximum reaction velocity which corresponds to 17 - 30% of decomposition of the preparation.

3. It is shown that the explosive decomposition of silver oxalate is a direct proof of its autocatalytic decomposition under the effect of a solid

reaction product.

4. It is established that the travel of electrons along a wire not connected with the crystal lattice of the silver oxalate, will not cause explosion of the preparation.

5. It is demonstrated that the autocatalytic process in topochemical reactions is caused by formation of the solid phase related with the crystal lattice of the initial substance.

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